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(54) **Process for producing lubricating base oils**

(57) Process for the preparation of lubricating base
oils having a VI of at least 150 from a Fischer-Tropsch
wax feed, which process comprises the steps of:

- (a) contacting the Fischer-Tropsch wax feed with a
hydroconversion catalyst under hydroconversion
conditions,
- (b) separating the hydroconverted effluent obtained
in step (a) into at least one lighter fraction and a
heavy fraction, and

(c) dewaxing the heavy fraction to yield the base oil,
wherein the Fischer-Tropsch wax feed has a con-
gealing point of at least 50 °C and has such boiling
range that the difference between the 90 %wt boil-
ing point and the 10 %wt boiling point ($T_{90}-T_{10}$) is
in the range of from 40 to 150 °C.

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Description

[0001] The present invention relates to a process for producing lubricating base oils from Fischer-Tropsch waxes, and in particular lubricating base oils having a viscosity index (VI) of at least 150.

[0002] Processes for producing base oils having VI's above 150 from Fischer-Tropsch waxes are known in the art. For instance, in EP-A-0,515,256 a process for producing such base oils is disclosed, said process comprising the steps of:

- (a) contacting the synthetic or Fischer-Tropsch wax with hydrogen in the presence of an alumina-based hydroconversion catalyst;
- (b) contacting the effluent of step (a) with a hydroisomerisation catalyst comprising a matrix, a specific zeolite Y and a hydrogenation component;
- (c) separating the effluent of step (b) into at least one lighter fraction and a heavy fraction; and
- (d) dewaxing the heavy fraction thereby yielding the base oil and a wax fraction. This wax fraction may be partly or totally recycled to hydro-isomerisation step (b).

[0003] The Fischer-Tropsch wax used as the feed in the working examples of EP-A-0,515,256 has a broad boiling range. The difference between 90 %wt boiling point and 10 %wt boiling point is as high as 249 °C. This implies that a large variety of paraffinic molecules is present in said wax. Due to the presence of such large variety of different paraffinic molecules, it will be very difficult to meet the specifications as regards volatility when the base oils produced should be used as lubricating base oils.

[0004] In US-A-4,943,672 a process is disclosed for producing lubricating base oils having a VI of at least 130 from Fischer-Tropsch waxes, in which process the wax is first hydrotreated under severe conditions, then the hydrotreated wax is hydro-isomerised by contacting it with a fluorided Group VIII (noble) metal-on-alumina catalyst, subsequently the effluent from the hydroisomerisation step is fractionated to produce a lubricating oil fraction and finally this lubricating oil fraction is dewaxed to produce the desired lubricating base oil. Unconverted wax recovered in the final dewaxing step may be recycled to the hydro-isomerisation step. The Fischer-Tropsch wax used should be a high boiling wax, since it is the intention to convert in the severe hydrotreating step that material present in the wax that has a boiling point above about 565 °C. In the Example of US-4,943,672 a Fischer-Tropsch wax is used which was obtained as the 370 °C+ fraction from the distillation of a Fischer-Tropsch synthesis product. Accordingly, the waxes used as the feedstocks are relatively high boiling waxes having a broad boiling range and a large heavy tail. Due to the broad boiling range and particularly due to the large heavy tail present in the wax, the fractionation after the

hydroisomerisation step, or -if applied- after the hydrofinishing step, should remove both the lightest fraction (boiling below 338 °C) and the heaviest fraction (boiling above 538 °C) from the hydroprocessed wax in order to obtain a final base oil product having acceptable volatility properties.

[0005] In US-A-5,059,299 a process for producing lubricating base oils having a VI of at least 130 and a pour point of -21 °C or lower from waxy feeds is disclosed, in which process the waxy feed -after an optional hydrotreating step- is first isomerised in an isomerisation zone at a predefined level of conversion, the total product of the isomerisation zone is then fractionated yielding a lube fraction boiling in the luboil range (i.e. above 330 °C and preferably above 370 °C) and this lube fraction is finally solvent dewaxed to yield the desired lubricating base oil and unconverted wax. This unconverted wax may be recycled to the isomerisation zone. The wax used as the feed may be a synthetic wax from a Fischer-Tropsch process or could be a slack wax obtained from a dewaxing process. No specific demands are made upon the Fischer-Tropsch waxes to be useful as a feed in the process disclosed. The Fischer-Tropsch wax used in Example 1 of US-A-5,059,299 is a high boiling wax having a relatively broad boiling range, which, as has already been stated above, results in the base oil product having unacceptable volatility properties. The isomerisation catalyst used suitably comprises a hydrogenating component on a halogenated refractory oxide support. The preferred catalyst is disclosed to be platinum on fluorided alumina.

[0006] Although the prior art processes perform satisfactory in many respects, there is still room for optimisation and improvement. The present invention aims to provide such improved process. More specifically, the present invention aims to provide a process for preparing base oils having a VI of at least 150 from a Fischer-Tropsch wax, which process involves a single hydroprocessing stage and a fractionation stage, wherein only the lighter components need to be removed from the hydroprocessed effluent. Furthermore, it is an object of the present invention to provide base oils having excellent properties, particularly in terms of VI and volatility, at commercially attractive yields.

[0007] It has been found that these objects can be effectively achieved by using as the feed a specific Fischer-Tropsch wax having a relatively narrow boiling range and meeting certain requirements as to its congealing point and wherein the dewaxing step is performed by means of catalytic dewaxing.

[0008] Accordingly, the present invention relates to a process for the preparation of lubricating base oils having a VI of at least 150 from a Fischer-Tropsch wax feed, which process comprises the steps of:

- (a) contacting the Fischer-Tropsch wax feed with a hydroconversion catalyst under hydroconversion conditions,

- (b) separating the hydroconverted effluent obtained in step (a) into at least one lighter fraction and a heavy fraction, and
- (c) catalytically dewaxing the heavy fraction to yield the base oil,

wherein the Fischer-Tropsch wax feed has a congealing point of at least 50 °C and has such boiling range that the difference between the 90 %wt boiling point and the 10 %wt boiling point ($T_{90}-T_{10}$) is in the range of from 40 to 150 °C.

[0009] The Fischer-Tropsch wax used as the feed for the present process, is obtained via the well-known Fischer-Tropsch hydrocarbon synthesis process. In general, such Fischer-Tropsch hydrocarbon synthesis involves the preparation of hydrocarbons from a mixture of carbon monoxide and hydrogen at elevated temperature and pressure in the presence of a suitable catalyst. The Fischer-Tropsch catalyst normally is selective for preparing paraffinic molecules, mostly straight-chain paraffins, and the product from a Fischer-Tropsch synthesis reaction therefore usually is a mixture of a large variety of paraffinic molecules. Those hydrocarbons that are gaseous or liquid at room temperature are recovered separately, for instance as fuel gas (C_5^-), solvent feedstocks and detergent feedstocks (up to C_{17}). The more heavy paraffins (C_{18+}) are recovered as one or more wax fractions, commonly referred to as Fischer-Tropsch wax(es) or synthetic wax(es). For the purpose of the present invention only those Fischer-Tropsch waxes are useful as the feed, which meet the aforementioned requirements with respect to their boiling range and congealing point.

[0010] Within the limits defined hereinbefore, preferred Fischer-Tropsch wax feeds are those having a congealing point in the range of from 55 to 150 °C, preferably from 60 to 120 °C and/or such boiling range that the $T_{90}-T_{10}$ is in the range of from 50 to 130 °C. Those Fischer-Tropsch waxes melting below 100 °C, suitably have a kinematic viscosity at 100 °C (V_{k100}) of at least 3 mm²/s, preferably between 3 and 12 mm²/s, more preferably between 4 and 10 mm²/s. Those Fischer-Tropsch waxes melting above 100 °C suitably have a kinematic viscosity at a temperature T, which is 10 to 20 °C higher than their melting point, in the range of from 8 to 15 mm²/s, preferably from 9 to 14 mm²/s.

[0011] The hydroconversion catalyst used in step (a) may in principle be any catalyst known in the art to be suitable for isomerising paraffinic molecules. In general, suitable hydroconversion catalysts are those comprising a hydrogenation component supported on a refractory oxide carrier, such as amorphous silica-alumina, alumina, fluorided alumina, molecular sieves (zeolites) or mixtures of two or more of these. One type of preferred catalysts to be applied in the hydroconversion step in accordance with the present invention are hydroconversion catalysts comprising platinum and/or palladium as the hydrogenation component. A very much

preferred hydroconversion catalyst comprises platinum and palladium supported on an amorphous silica-alumina (ASA) carrier. The platinum and/or palladium is suitably present in an amount of from 0.1 to 5.0% by weight, more suitably from 0.2 to 2.0% by weight, calculated as element and based on total weight of carrier. If both present, the weight ratio of platinum to palladium (calculated as element) may vary within wide limits, but suitably is in the range of from 0.05 to 10, more suitably 0.1 to 5. Examples of suitable noble metal on ASA catalysts are, for instance, disclosed in WO-A-94/10264 and EP-A-0,582,347. Other suitable noble metal-based catalysts, such as platinum on a fluorided alumina carrier, are disclosed in e.g. US-A-5,059,299 and WO-A-92/20759.

[0012] A second type of suitable hydroconversion catalysts are those comprising at least one Group VIB metal, preferably tungsten and/or molybdenum, and at least one non-noble Group VIII metal, preferably nickel and/or cobalt, as the hydrogenation component. Usually both metals are present as oxides, sulphides or a combination thereof. The Group VIB metal is suitably present in an amount of from 1 to 35% by weight, more suitably from 5 to 30% by weight, calculated as element and based on total weight of catalyst. The non-noble Group VIII metal is suitably present in an amount of from 1 to 25 %wt, preferably 2 to 15 %wt, calculated as element and based on total weight of carrier. A hydroconversion catalyst of this type which has been found particularly suitable is a catalyst comprising nickel and tungsten supported on fluorided alumina.

[0013] A third class of suitable hydroconversion catalysts are those based on an intermediate pore size zeolitic material, suitably comprising at least one Group VIII metal component, preferably Pt and/or Pd, as the hydrogenation component. Suitable zeolitic materials, then, include ZSM-5, ZSM-22, ZSM-23, ZSM-35, SSZ-32, ferrierite, zeolite beta, mordenite and silica-aluminophosphates, such as SAPO-11 and SAPO-31. Examples of suitable hydroisomerisation catalysts are, for instance, described in WO-A-92/01657.

[0014] The hydroconversion conditions applied in step (a) are those known to be suitable in hydro-isomerisation operations. Suitable conditions, then, involve operating temperatures in the range of from 275 to 450 °C, preferably 300 to 425 °C, a hydrogen partial pressure in the range of from 10 to 250 bar, suitably 25 to 200 bar, a weight hourly space velocity (WHSV) in the range of from 0.1 to 10 kg/l/h, preferably 0.2 to 5 kg/l/h, and a gas rate in the range of from 100 to 5,000 NI/kg, preferably 500 to 3,000 NI/kg.

[0015] In step (b) of the present process the hydroconverted effluent from step (a) is separated into at least one lighter fraction and a heavy fraction. The effective cutpoint of the heavy fraction is suitably in the range of from 325 to 450 °C and even more suitably is in the range of from 350 to 420 °C, particularly when the lubricating base oils to be obtained are to be used in engine

oils. The effective cutpoint of the heavy fraction is the temperature above which at least at least 85% by weight and preferably at least 90% by weight, of the hydrocarbons present in this heavy fraction has its boiling point. This separation or fractionation can be achieved by techniques known in the art, such as atmospheric and vacuum distillation or vacuum flashing.

[0016] The heavy fraction obtained in step (b) is subsequently subjected to a dewaxing treatment in step (c) to arrive at the desired pour point. The dewaxing carried out in step (c) may in principle be carried out via any known dewaxing process. Examples of suitable dewaxing operations are the conventional solvent dewaxing processes, particularly those wherein methylethylketone, toluene or a mixture thereof is used as the dewaxing solvent, and the catalytic dewaxing processes. Both types of dewaxing operations are well known in the art. The most commonly applied solvent dewaxing process is the methyl ethyl ketone (MEK) solvent dewaxing route, wherein MEK is used as the dewaxing solvent, possibly in admixture with toluene. Catalytic dewaxing generally involves cracking and/or isomerising linear and slightly branched paraffinic hydrocarbon molecules -which negatively influence the cold flow properties of the base oil- in the presence of hydrogen and a dewaxing catalyst under appropriate dewaxing conditions. Suitable dewaxing catalysts which mainly favour cracking of paraffinic hydrocarbons are those comprising ZSM-5, ferrierite and/or silicalite and optionally a hydrogenation component. Examples of catalysts which mainly favour isomerisation of linear or slightly branched hydrocarbons, include catalysts comprising a silicoaluminophosphate (SAPO), such as e.g. SAPO-11, SAPO-31 and SAPO-41, ZSM-23 and SSZ-32. Another class of suitable dewaxing catalysts for use in dewaxing step (c) are those catalysts based on a molecular sieve having pores with a diameter in the range of from 0.35 to 0.80 nm and containing covalently bound alumina moieties in its framework, which molecular sieve has been modified to reduce the mole percentage of alumina, suitably by a surface dealumination treatment. This type of catalysts and dewaxing operations wherein such catalysts are used, are disclosed in European patent application EP-A-832171. Accordingly, a particularly suitable class of dewaxing catalysts comprise a hydrogenation component supported on surface deactivated molecular sieve and optionally a low acidity refractory oxide binder material. The hydrogenation component may comprise at least one Group VIB metal component, for example one or more of tungsten, molybdenum and chromium and/or at least one Group VIII metal component, for example one or more of palladium, platinum, nickel and cobalt. It has been found particularly preferred for the purpose of the present invention to employ a hydrogenation component comprising platinum and/or palladium, suitably present in an amount of from 0.2 to 3.0% by weight as calculated as element and based on total weight of support, i.e. modified molecular sieve plus op-

tional binder. Suitable molecular sieves include MFI-type zeolites, such as ZSM-5 and silicalite, offretite, ferrierite, ZSM-35 and zeolites of the MTT-type, such as ZSM-23 and SSZ-32. Of these, the MTT-type zeolites, ferrierite, ZSM-5 and mixtures thereof are preferred for the purpose of the present invention. If present at all, suitable binder materials include low acidity refractory oxides such as silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these with silica being most preferred. The weight ratio of surface deactivated molecular sieve to binder may range from 10/90 to 100/0.

[0017] The slack wax obtained in the dewaxing treatment of step (c) is suitably recycled, i.e. all or part of this slack wax is routed back to the hydroconversion step (a), most conveniently by blending it with the fresh Fischer-Tropsch wax feed. In this way the final yield of lubricating base oil can be maximised.

[0018] The lubricating base oils obtained by the process according to the present invention can be used in a variety of oils. For instance, those lubricating base oils obtained from Fischer-Tropsch waxes having a T_{90} between about 400 and 500 °C are very useful in electrical oils, transformer oils and refrigerator oils. Those base oils obtained from Fischer-Tropsch waxes having a T_{90} above 450 °C, suitably between 450 and 575 °C, are very useful as lubricating base oils used for the more sophisticated lubricants required in, for instance, automotive engines.

[0019] The invention is now further illustrated by the following examples without restricting the scope of the invention to these specific embodiments.

Comparative Example 1

[0020] A Fischer-Tropsch wax having the properties as listed in Table I was contacted with a fluorided NiW/ alumina catalyst (5.0 %wt Ni, 23.1 %wt W, 4.6 %wt F, all based on total weight of carrier) at a temperature of 383 °C, a hydrogen partial pressure of 140 bar, a WHSV of 1 kg/l/h and a gas rate of 1,500 Ni/kg. The effluent was fractionated and the 390 °C+ fraction (obtained at a yield of 87.8% by weight based on total effluent) was subsequently solvent dewaxed using MEK/toluene at -20 °C. The resulting base oil had a VI of 165, a pour point of -15 °C, a kinematic viscosity at 100 °C (V_{k100}) of 4.95 mm²/s and a Noack volatility (as determined by CEC-L-40-T87) of 8.3% by weight. Total yield of lubricating base oil amounted up to 41% by weight based on Fischer-Tropsch wax feed.

TABLE I

Properties of Fischer-Tropsch wax	
T_{10} (°C)	432
T_{50} (°C)	482
T_{90} (°C)	527

TABLE I (continued)

Properties of Fischer-Tropsch wax	
$T_{90}-T_{10}$ (°C)	95
CPt (°C)	69
Vk100 (mm ² /s)	5.67

Comparative Example 2

[0021] The same Fischer-Tropsch wax as used in Example 1 was contacted with a PtPd/ASA (0.3 %wt Pt, 1 %wt Pd, ASA: silica/alumina molar ratio is 55/45) catalyst at a temperature of 332 °C, whilst the other conditions were the same as applied in Example 1. The effluent was fractionated and the 390 °C+ fraction (obtained at a yield of 88.3% by weight based on total effluent) was subsequently solvent dewaxed using MEK/toluene at -20 °C. The resulting base oil had a VI of 167, a pour point of -15 °C, a kinematic viscosity at 100 °C (Vk100) of 4.86 mm²/s and a Noack volatility of 7.4% by weight. Total yield of lubricating base oil amounted up to 39% by weight based on Fischer-Tropsch wax feed.

Example 3 according to the invention

[0022] The procedure of Example 1 was repeated except that the 390 °C+ fraction obtained was catalytically dewaxed instead of solvent dewaxed. Catalytic dewaxing was carried out by passing said 390 °C+ fraction over a dewaxing catalyst comprising 0.7% by weight of Pt on surface dealuminated ZSM-23 (surface dealumination carried out according to the method disclosed in U.S. Patent No. 5,157,191 using ammonium hexafluoro-silicate) at a temperature of 310 °C, a hydrogen partial pressure of 40 bar, a WHSV of 1 kg/l/h and a gas rate of 693 NI/kg.

[0023] The resulting base oil had a VI of 151, a pour point of -27 °C, a kinematic viscosity at 100 °C (Vk100) of 4.96 mm²/s and a Noack volatility (as determined by CEC-L-40-T87) of 8.8% by weight. Total yield of lubricating base oil amounted up to 62.4% by weight based on Fischer-Tropsch wax feed.

Claims

1. Process for the preparation of lubricating base oils having a VI of at least 150 from a Fischer-Tropsch wax feed, which process comprises the steps of:

- (a) contacting the Fischer-Tropsch wax feed with a hydroconversion catalyst under hydro-conversion conditions,
- (b) separating the hydroconverted effluent obtained in step (a) into at least one lighter fraction and a heavy fraction, and

(c) catalytic dewaxing the heavy fraction to yield the base oil,

wherein the Fischer-Tropsch wax feed has a congealing point of at least 50 °C and has such boiling range that the difference between the 90 %wt boiling point and the 10 %wt boiling point ($T_{90}-T_{10}$) is in the range of from 40 to 150 °C.

2. Process according to claim 1, wherein $T_{90}-T_{10}$ is in the range of from 50 to 130 °C.
3. Process according to claim 1 or 2, wherein the Fischer-Tropsch wax feed has a congealing point in the range of from 55 to 150 °C, preferably from 60 to 120 °C.
4. Process according to any one of the preceding claims, wherein the hydroconversion catalyst comprises a hydrogenation component supported on a refractory oxide carrier.
5. Process according to claim 4, wherein the hydro-conversion catalyst comprises platinum and/or palladium as the hydrogenation component.
6. Process according to claim 5, wherein the hydro-conversion catalyst comprises platinum and palladium supported on an amorphous silica-alumina carrier.
7. Process according to claim 4, wherein the hydro-conversion catalyst comprises at least one Group VIB metal, preferably tungsten, and at least one non-noble Group VIII metal, preferably nickel, as the hydrogenation component.
8. Process according to any one of the preceding claims, wherein the heavy fraction is obtained in step (b) at an effective cutpoint in the range of from 350 to 420 °C.
9. Process according to any one of claims 1-8, wherein the catalytic dewaxing is performed using a catalyst comprising MFI-type, offretite, ferrierite, or MTT-type zeolites and a Group VIII metal.
10. Process according to claim 9, wherein the Group VIII metal is platinum and/or palladium, present in an amount of from 0.2 to 3.0% by weight.



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EUROPEAN SEARCH REPORT

Application Number
EP 03 07 7527

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Place of search The Hague		Date of completion of the search 3 October 2003	Examiner De Herdt, O.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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(54) **Biodegradable high performance hydrocarbon base oils**

(57) Discloses novel biodegradable high performance hydrocarbon base oils useful as lubricants in engine oil and industrial compositions, and process for their manufacture. A waxy, or paraffinic feed, particularly a Fischer-Tropsch wax, is reacted over a dual function catalyst to produce hydroisomerization and hydrocracking reactions, at 700 °F+ conversion levels ranging from about 20 to 50 wt.%, preferably about 25-40 wt.%, sufficient to produce a crude fraction, e.g., a C₅-1050 °F+ crude fraction, containing 700 °F+ isoparaffins having

from about 6.0 to about 7.5 methyl branches per 100 carbon atoms in the molecule. The methyl paraffins containing crude fraction is topped via atmospheric distillation to produce a bottoms fraction having an initial boiling point between about 650 °F and 750 °F which is then solvent dewaxed, and the dewaxed oil is then fractionated under high vacuum to produce biodegradable high performance hydrocarbon base oils.

Description**1. Field of the Invention**

5 [0001] This invention relates to biodegradable high performance hydrocarbon base oils, suitable as engine oil and industrial oil compositions. In particular, it relates to lubricant base oil compositions, and process for making such compositions by the hydroisomerization/hydrocracking of paraffinic waxes, suitably Fischer-Tropsch waxes.

2. Background

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[0002] It is well known that very large amounts of lubricating oils, e.g., engine oils, transmission oils, gear box oils, etc., find their way into the natural environment, accidentally and even deliberately. These oils are capable of causing much environmental harm unless they are acceptably biodegradable. For this reason there is increasing emphasis in this country, and abroad, to develop and employ high performance lubricant base oils which are environmentally friendly, or substantially biodegradable on escape or release into the environment.

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[0003] Few hydrocarbon base oils are environmentally friendly though their qualities as lubricants may be unchallenged. The literature stresses the superior biodegradability of ester based lubricants, natural and synthetic, over hydrocarbon based products. However there is little or no emphasis on performance. Few references are found relating to the biodegradability of hydrocarbon lubricants. Ethyl Petroleum Additives's EP 468 109A however does disclose the biodegradability of lubricating oils containing at least 10 volume percent of a "biodegradable liquid hydrocarbon of lubricating viscosity formed by oligomerization of a 1-alkene hydrocarbon having 6 to 20 carbon atoms in the molecule and hydrogenation of the resultant oligomer." Apparently hydrogenated oligomers of this type have unexpectedly high biodegradability, particularly those having at least 50 volume percent dimer, trimer and/or tetramer. Ethyl Petroleum Additive's EP 558 835 A1 discloses lubricating oils having similar polyalphaolefin, PAO, components. However, both

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[0004] There is a clear need for biodegradable high performance hydrocarbon base oils useful as engine oil and industrial oil, or lubricant compositions which are at least equivalent to the polyalphaolefins in quality, but have the distinct advantage of being more biodegradable.

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3. Summary of the Invention

[0005] This invention, which supplies these and other needs, accordingly relates to biodegradable high performance paraffinic lubricant base oils, and process for the production of such compositions by the hydrocracking and hydroisomerization of paraffinic, or waxy hydrocarbon feeds, especially Fischer-Tropsch waxes or reaction products, all or at least a portion of which boils above 700°F, i.e., 700°F+. The waxy feed is first contacted, with hydrogen, over a dual functional catalyst to produce hydroisomerization and hydrocracking reactions sufficient to convert at least about 20 percent to about 50 percent, preferably from about 25 percent to about 40 percent, on a once through basis based on the weight of the 700°F+ feed, or 700°F+ feed component, to 700°F- materials, and produce 700°F+ materials rich in methyl-paraffins. This resultant crude product, which contains both 700°F- and 700°F+ materials, characterized generally as a C₅-1050°F+ crude fraction, is first topped via atmospheric distillation to produce a lower boiling fraction the upper end of which boils between about 650°F and 750°F, e.g., 700°F, and a higher boiling, or bottoms fraction having an initial boiling point ranging between about 650°F and 750°F, e.g., 700°F, and an upper end or final boiling point of about 1050°F+, e.g., a 700°F+ fraction. The lower boiling fraction, e.g., the 700°F- fraction, from the distillation is a non-lube, or fuel fraction.

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[0006] At these conversion levels, the hydroisomerization/hydrocracking reactions converts a significant amount of the waxy, or paraffinic feed to 700°F+ methyl-paraffins, i.e., isoparaffins containing one or more methyl groups in the molecule, with minimal formation of branches of carbon number greater than 1; i.e., ethyl, propyl, butyl or the like. The 700°F+ bottoms fractions so-treated contain 700°F+ isoparaffins having from about 6.0 to about 7.5 methyl branches per 100 carbon atoms, preferably from about 6.5 to about 7.0 methyl branches per 100 carbon atoms, in the molecule. These isoparaffins, contained in a mixture with other materials, provide a product from which high performance, highly biodegradable lube oils can be obtained.

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[0007] The higher boiling bottoms fractions, e.g., the 700°F+ bottoms fraction containing the methyl-paraffins, or crude fraction, is dewaxed in a conventional solvent dewaxing step to remove n-paraffins, and the recovered dewaxed product, or dewaxed oil, is fractionated under vacuum to produce paraffinic lubricating oil fractions of different viscosity grades, including hydrocarbon oil fractions suitable as high performance engine oils and engine lubricants which, unlike most hydrocarbon base oils, are biodegradable on release or escape into the environment. In terms of their performance

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they are unsurpassed by the PAO lubricants, and are superior thereto in terms of their biodegradability.

4. Detailed Description

[0008] The feed materials that are isomerized to produce the lube base stocks, and lubricants with the catalyst of this invention are waxy feeds, i.e., C_5+ , preferably having an initial boiling point above about 350°F (117°C), more preferably above about 550°F (288°C), and contain a major amount of components boiling above 700°F (370°C). The feed may be obtained either from a Fischer-Tropsch process which produces substantially normal paraffins, or from petroleum derived slack waxes.

[0009] Slack waxes are the by-products of dewaxing operations where a diluent such as propane or a ketone (e.g., methylethyl ketone, methyl isobutyl ketone) or other diluent is employed to promote wax crystal growth, the wax being removed from the base oil by filtration or other suitable means. The slack waxes are generally paraffinic in nature, boil above about 600°F (316°C), preferably in the range of 600°F (316°C) to about 1050°F (566°C), and may contain from about 1 to about 35 wt.% oil. Waxes with low oil contents, e.g., 5-20 wt.% are preferred; however, waxy distillates or raffinates containing 5-45% wax may also be used as feeds. Slack waxes are usually freed of polynuclear aromatics and hetero-atom compounds by techniques known in the art; e.g., mild hydrotreating as described in U.S. Patent No. 4,900,707, which also reduces sulfur and nitrogen levels preferably to less than 5 ppm and less than 2 ppm, respectively. Fischer-Tropsch waxes are preferred feed materials, having negligible amounts of aromatics, sulfur and nitrogen compounds. The Fischer-Tropsch liquid, or wax, is characterized as the product of a Fischer-Tropsch process wherein a synthetic gas, or mixture of hydrogen and carbon monoxide, is processed at elevated temperature over a supported catalyst comprised of a Group VIII metal, or metals, of the Periodic Table of The Elements (Sargent-Welch Scientific Company, Copyright 1968), e.g., cobalt, ruthenium, iron, etc. The Fischer-Tropsch wax contains C_5+ , preferably $C_{10}+$, more preferably $C_{20}+$ paraffins. A distillation showing the fractional make up (± 10 wt.% for each fraction) of a typical Fischer-Tropsch process liquid feedstock is as follows:

Boiling Temperature Range	Wt.% of Fraction
IBP - 320°F	13
320 - 500°F	23
500 - 700°F	19
700 - 1050°F	34
1050°F+	11
	<u>100</u>

[0010] The wax feed is contacted, with hydrogen, at hydrocracking/hydroisomerization conditions over a bifunctional catalyst, or catalyst containing a metal, or metals, hydrogenation component and an acidic oxide support component active in producing both hydrocracking and hydroisomerization reactions. Preferably, a fixed bed of the catalyst is contacted with the feed at conditions which convert about 20 to 50 wt.%, preferably about 25 to 40 wt.%, of the 700°F components of the feed to 700°F- materials and produce a lower boiling fraction having an upper end boiling point between about 650°F and 750°F, e.g., 700°F, and a higher boiling, or bottoms fraction having an initial boiling point between about 650°F and 750°F, e.g., 700°F, the higher boiling fraction that remains containing high quality blending components for the production of high performance biodegradable base oils. In general, the hydrocracking/catalyst hydroisomerization reaction is conducted by contacting the waxy feed over the at a controlled combination of conditions which produce these levels of conversion; i.e., by selection of temperatures ranging from about 400°F to about 850°F, preferably from about 500°F to about 700°F, pressures ranging generally from about 100 pounds per square inch gauge (psig) to about 1500 psig, preferably from about 300 psig to about 1000 psig, hydrogen treat gas rates ranging from about 1000 SCFB to about 10,000 SCFB, preferably from about 2000 SCFB to about 5000 SCFB, and space velocities ranging generally from about 0.5 LHSV to about 10 LHSV, preferably from about 0.5 LHSV to about 2.0 LHSV.

[0011] The active metal component of the catalyst is preferably a Group VIII metal, or metals, of the Periodic Table Of The Elements (Sargent-Welch Scientific Company Copyright 1968) in amount sufficient to be catalytically active for hydrocracking and hydroisomerization of the waxy feed. The catalyst may also contain, in addition to the Group VIII metal, or metals, a Group IB and/or a Group VIB metal, or metals, of the Periodic Table. Generally, metal concentrations range from about 0.05 percent to about 20 percent, based on the total weight of the catalyst (wt.%), preferably from about 0.1 wt. percent to about 10 wt. percent. Exemplary of such metals are such non-noble Group VIII metals as nickel and cobalt, or mixtures of these metals with each other or with other metals, such as copper, a Group IB metal, or molybdenum, a Group VIB metal. Palladium and platinum are exemplary of suitable Group VIII noble metals. The metal, or metals, is incorporated with the support component of the catalyst by known methods, e.g., by impregnation

of the support with a solution of a suitable salt or acid of the metal, or metals, drying and calcination.

[0012] The catalyst support is constituted of metal oxide, or metal oxides, components at least one component of which is an acidic oxide active in producing olefin cracking and hydroisomerization reactions. Exemplary oxides include silica, silica-alumina, clays, e.g., pillared clays, magnesia, titania, zirconia, halides, e.g., chlorided alumina, and the like. The catalyst support is preferably constituted of silica and alumina, a particularly preferred support being constituted of up to about 35 wt.% silica, preferably from about 2 wt.% to about 35 wt.% silica, and having the following pore-structural characteristics:

Pore Radius, Å	Pore Volume
0-300	>0.03 ml/g
100-75,000	<0.35 ml/g
0-30	<25% of the volume of the pores with 0-300 Å radius
100-300	<40% of the volume of the pores with 0-300 Å radius

The base silica and alumina materials can be, e.g., soluble silica containing compounds such as alkali metal silicates (preferably where $\text{Na}_2\text{O}:\text{SiO}_2 = 1:2$ to $1:4$), tetraalkoxy silane, orthosilic acid ester, etc.; sulfates, nitrates, or chlorides of aluminum alkali metal aluminates; or inorganic or organic salts of alkoxides or the like. When precipitating the hydrates of silica or alumina from a solution of such starting materials, a suitable acid or base is added and the pH is set within a range of about 6.0 to 11.0. Precipitation and aging are carried out, with heating, by adding an acid or base under reflux to prevent evaporation of the treating liquid and change of pH. The remainder of the support producing process is the same as those commonly employed, including filtering, drying and calcination of the support material. The support may also contain small amounts, e.g., 1-30 wt.%, of materials such as magnesia, titania, zirconia, hafnia, or the like.

[0013] Support materials and their preparation are described more fully in U.S. Patent No. 3,843,509 incorporated herein by reference. The support materials generally have a surface area ranging from about 180-400 m^2/g , preferably 230-375 m^2/g , a pore volume generally of about 0.3 to 1.0 ml/g, preferably about 0.5 to 0.95 ml/g, bulk density of generally about 0.5-1.0 g/ml, and a side crushing strength of about 0.8 to 3.5 kg/mm.

[0014] The hydrocracking/hydroisomerization reaction is conducted in one or a plurality of reactors connected in series, generally from about 1 to about 5 reactors; but preferably the reaction is conducted in a single reactor. The waxy hydrocarbon feed, e.g., Fischer-Tropsch wax, preferably one boiling above about 700°F, or has a large amount of 700°F+ hydrocarbon components, is fed, with hydrogen, into the reactor, a first reactor of the series, to contact a fixed bed of the catalyst at hydrocracking/hydro-isomerization reaction conditions to hydrocrack, hydroisomerize and convert at least a portion of the waxy feed to products which include after further work up high quality oils and lube blending components.

[0015] The following examples are illustrative of the more salient features of the invention. All parts, and percentages, are given in terms of weight unless otherwise specified.

Examples 1-9

[0016] A mixture of hydrogen and carbon monoxide synthesis gas ($\text{H}_2:\text{CO}$ 2.11-2.16) was converted to heavy paraffins in a slurry Fischer-Tropsch reactor. A titania supported cobalt rhenium catalyst was utilized for the Fischer-Tropsch reaction. The reaction was conducted at 422-428°F, 287-289 psig, and the feed was introduced at a linear velocity of 12 to 17.5 cm/sec. The alpha of the Fischer-Tropsch synthesis step was 0.92. The paraffinic Fischer-Tropsch product was isolated in three nominally different boiling streams; separated by utilizing a rough flash. The three boiling fractions which were obtained were: 1) a C_5 -500°F boiling fraction, i.e., F-T cold separator liquids; 2) a 500-700°F boiling fraction, i.e., F-T hot separator liquids; and 3) a 700°F+ boiling fraction, i.e., a F-T reactor wax.

[0017] A series of base oils were prepared in runs made by hydrocracking and isomerizing the 700°F+ Fischer-Tropsch reactor wax feedstock, with hydrogen, at different levels of conversion over a silica exchanced cobalt-moly-nickel catalyst (CoO , 3.6 wt.%; MoO_3 , 16.4 wt.%; NiO , 0.66 wt.%; on a $\text{SiO}_2\text{-Al}_2\text{O}_3$ support, 13.7 wt.% of which is silica); having a surface area of 270 m^2/g , and pore volume <30 mm equal to 0.43). A combination of reaction conditions, i.e., as relates to temperature, space velocity, pressure and hydrogen treat rate, to convert 30 wt.%, 35 wt.%, 45 wt.%, 50 wt.%, 58 wt.%, 67 wt.%, and 80 wt.% respectively, of the feedstock to materials boiling below 700°F, i.e., 700°F-. The conditions for each of the respective runs and the yields which were obtained for each are given in Table 1. The Table also lists the amounts of IBP-650°F and 650°F+ products obtained by 15/5 distillation.

TABLE I
CONVERSION TO 700°F-, wt. %

	30	35	45	50	58	67	80
<u>Operating Conditions</u>							
Temperature, °F	681.9	689	705.2	701.5	709.7	707.1	711.4
Space Velocity, LHSV	0.42	0.50	0.50	0.45	0.50	0.43	0.44
Pressure, psig	--	--	1000	--	--	--	--
H ₂ Treat Rate, SCF/B	--	--	2500	--	--	--	--
<u>Yields (wt. % recovery)</u>							
C ₁ -C ₄	1.17	0.73	1.73	2.11	2.14	2.43	3.70
C ₅ -320°F	5.48	3.11	9.68	9.75	9.48	14.93	23.10
320-550°F	10.43	10.11	17.82	17.92	22.87	25.20	27.04
550-700°F	20.48	23.94	21.88	24.63	27.81	28.01	30.21
700°F+	62.44	62.11	48.89	45.59	37.70	29.43	15.93
15/5 Composite							
<u>Distillation (wt. %)</u>							
IBP-650°F	32.25	26.71	37.46	44.26	48.35	59.80	67.77
650°F+	67.75	73.29	62.54	55.74	51.65	40.20	32.23

[0018] A 650°F+ bottom fraction was recovered from the products obtained from each of the runs by atmospheric distillation, and then again fractionated under high vacuum to produce several viscosity grades of lubricant, viz. 60N, 100N, 175N and about 350-400N. The residual products were then subjected to solvent dewaxing to remove waxy hydrocarbons and lower the pour point to about -18°C (32°F).

[0019] For each viscosity grade, the dewaxing conditions were held constant so that the effect of conversion level on dewaxing could be evaluated. The dewaxing conditions for 100N and 175N viscosity grades at the 30%, 50%, 67% and 80% conversion levels are given in Table 2.

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Table 2

Dewaxing Conditions ¹		
	Viscosity Grade	
	100N	175N
30% Conversion		
Solvent:Oil Ratio	3:1	3:1
Filter Temp, °C	-21	-21
Pour Pt, °C	-18	-18
50% Conversion		
Solvent:Oil Ratio	3:1	3:1
Filter Temp, °C	-21	-21
Pour Pt, °C	-21	-21
67% Conversion		
Solvent:Oil Ratio	3:1	3:1
Filter Temp, °C	-21	-21
Pour Pt, °C	-15	-18
80% Conversion		
Solvent:Oil Ratio	3:1	3:1
Filter Temp, °C	-21	-21
Pour Pt, °C	-24	-24

¹ All dewaxings employed 100% methylisobutylketone, MIBK.

[0020] The physical properties, yields of dewaxed oil, DWO, and corresponding dry wax contents (both as wt.% on waxy feed) for each dewaxing in terms of the 100N and 175N viscosity grades at specific levels of conversion are given in Table 3.

TABLE 3
DEWAXED BASE OIL PHYSICAL PROPERTIES
VISCOSITY GRADES

	30% Conversion		50% Conversion		67% Conversion		80% Conversion	
	100N	175N	100N	175N	100N	175N	100N	175N
DeWaxed Oil Yield/Dry Wax Content (wt.% on waxy feed)	80.7/17.6	75.3/21.4	93.0/6.6	91.1/7.7	97/2.4	92/5.2	98/2.0	
Pour/Cloud Pt., °C	-18/-14	-18/-14	-21/-14	-21/-17	-15/-7	-18/-14	-24/-21	-24/-21
Density @ 15°C, kg/dm	0.8143	0.8218	0.8153	0.8229	0.8147	0.8231	0.8160	0.8234
Refractive Index @ 20°C								
Viscosity, cSt								
@ 40°C	15.59	26.96	16.28	29.14	15.90	28.76	16.71	18.94
@ 100°C	3.81	5.59	3.86	5.77	3.77	5.68	3.85	5.61
Viscosity Index	141	153	133	145	129	143	124	136
GCD, °C								
IBP	346	380	343	390	347	394	351	393
5%	369	408	367	418	369	419	370	416
50%	426	471	424	473	421	469	421	466
95%	486	535	488	531	479	524	478	523
FRP	522	567	528	565	515	558	513	559

[0021] Nuclear magnetic resonance (NMR) branching densities for 100N base oils produced at 30%, 50%, 67%, and 80% levels, respectively, are given in Table 4. It will be observed that the lower levels of methyl branching occurs at

the lower conversion levels; with the biodegradability of the oil increasing at the lower levels of conversion. Compositions of highest biodegradability are thus produced at the 30 wt.% level of conversion, and the next highest biodegradability compositions are produced at the 50 wt.% conversion level.

Table 4

100N Base Oil, ¹³ CNMR Branching Densities -----% Conversion-----				
Base Oil	30	50	67	80
V.I.	141	133	129	124
Per 100 Carbons Methyl Groups (CH ₃)	6.8	7.5	7.5	7.8

[0022] It is also found that the viscosity index, VI, decreases with increasing level of conversion for each specific viscosity grade. This is because base oils prepared at higher conversion levels tend to be more highly branched and consequently have lower viscosity indexes. For the 100N base oils, the VI ranges from 141 to 118. For the 175N oils, the corresponding VI range is 153 to 136, respectively. The 175N base oils have VIs which are also comparable to the commercial ETHYLFLO 166 which has a VI of 143. The VI of the 100N viscosity grade is comparable to the commercial ETHYLFLO 164 which has a VI of 125. For purposes of comparison, certain physical properties of the commercial 100N ETHYLFLO 164 and 175N ETHYLFLO 166 are presented in Table 5.

Table 5

ETHYLFLO™ 164	
(Lot 200-128)	
Viscosity at 100°C, cSt	3.88
Viscosity at 40°C, cSt	16.9
Viscosity at -40°C, cSt	2450
Viscosity Index	125
Pour Point, °C	-70
Flash Point (D-92), °C	217
NOACK volatility, %	11.7
CEC-L-33-T-82	30%
ETHYLFLO™ 166	
(Lot 200-122)	
Viscosity at 100°C, cSt	5.98
Viscosity at 40°C, cSt	30.9
Viscosity at -40°C, cSt	7830
Pour Point, °C	-64
Flash Point (D-92), °C	235
NOACK VOLATILITY, %	6.1
Viscosity Index	143
CEC-L-33-T-82	29%

[0023] To determine the biodegradability of the DWO base stocks, and lubricant compositions, tests were conducted in accordance with CEC-L-33-T-82, a test method developed by the Coordinating European Council (CEC) and reported in "Biodegradability Of Two-Stroke Cycle Outboard Engine Oils In Water: Tentative Test Method" pp 1-8 and incorporated herein by reference. The test measures the decrease in the amount of a substrate due to microbial action. It has been shown, as measured by CEC-L-33-T-82 that the DWO base stocks, and lubricant compositions produced in accordance with this invention are of biodegradability above about 50%, and 10 are generally above about 50% to about 90%, and higher, biodegradable.

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Examples 10-13

[0024] The CEC-L-33-T-82 test was run to observe the biodegradation of the following samples over a 21 day period, to wit:

Samples:

[0025]

A: Base Oil 100N, 30 wt.% Conv. - 1.5133 g/100 mL FREON
 B: Base Oil 100N, 50 wt.% Conv. - 1.4314 g/100 mL FREON
 C: Base Oil 100N, 67 wt.% Conv. - 1.5090 g/100 mL FREON
 D: Base Oil 100N, 80 wt.% Conv. - 1.5388 g/100 mL FREON
 X: VISTONE A30 - 1.4991 g/100 mL FREON

(Positive Calibration Material)

[0026] Each of the tests were conducted using a FREON solvent, and the stock solutions used were standard as required by the test procedure.

[0027] The inoculum used was non-filtered primary effluent from the Pike Brook Treatment Plant in Bellemead, New Jersey. The inoculum was determined to have between 1×10^4 and 1×10^5 colony forming units/mL (CFU/mL) by Easicult-TCC dip slides.

[0028] Triplicate test systems for all test materials and Vistone A30 were prepared and analyzed on day zero for parent material concentration. All extractions were performed as described in the test procedure. The analyses were performed on the Nicolet Model 205 FT-IR. Triplicate test systems for samples B through X, in addition to poisoned systems of each sample were placed on orbital shakers and continuously agitated at 150 rpm in total darkness at $25 \pm 0^\circ\text{C}$ until day twenty-one. On day twenty-one the samples were analyzed for residual parent material. Sample "A" was also evaluated at the day seven interval to determine removal rate along with the above mentioned samples. Triplicate systems for "A" were prepared, extracted and analyzed after seven, fourteen and twenty-one days of incubation.

RESULTS		
100N BASE OILS		
SAMPLE Level of Conversion	% BIODEGRADATION (21 DAYS)	STANDARD DEVIATION, SD
A: Base Oil 30 wt.%	84.62	1.12
B: Base Oil 50 wt.%	77.95	0.86
C: Base Oil 67 wt.%	73.46	1.01
D: Base Oil 80 wt.%	73.18	2.34
E. ETHYLFLO 164	30.00	0.54
X: VISTONE A30	98.62	1.09
¹ Based on analysis of triplicate inoculated test systems and triplicate poisoned test systems.		

RATE STUDY SAMPLE A		
DAY	% BIODEGRADATION	SD
7	76.15	2.74
14	82.82	2.37
21	84.62	1.12

Examples 14-16

[0029] The CEC-L-33-T-82 test was run to observe the biodegradation of the following test materials over a 21 day period.

Samples:

[0030]

A:¹ Base Oil 175N, 30 wt.% Conv. - 1.58 g/100 mL FREON

B:² Base Oil 175N, 50 wt.% Conv. - 1.09 g/100 mL FREON

C:¹ Base Oil 175N, 80 wt.% Conv. - 1.43 g/100 mL FREON

X:¹ VISTONE A30 - 1.5 g/100 mL FREON

(Positive Calibration Material)

¹ 500 μ L used to dose test systems to achieve \approx 7.5 mg loading of test material.

² 750 μ L used to dose test systems to achieve \approx 7.5 mg loading of test material.

[0031] Each of the tests were conducted using a FREON solvent, and the stock solutions used were standard as required by the test procedure.

[0032] The inoculum was non-filtered primary effluent from the Pike Brook Treatment Plant in Bellemead, New Jersey. The inoculum was determined to have between 1×10^4 and 1×10^5 colony forming units/mL (CFU/mL) by Easicult-TCC dip slides.

[0033] Triplicate test systems for all test materials and Vistone A30 were prepared and analyzed on day zero for parent material concentration. All extractions were performed as described in the test procedure. The analyses were performed on the Nicolet Model 205 FT-IR. Triplicate test systems for samples A through X, in addition to poisoned systems of each sample were placed inside environmental chambers and continuously agitated at 150 rpm in total darkness at $25 \pm 0^\circ\text{C}$ until day twenty-one. On day twenty-one the samples were analyzed for residual parent material.

RESULTS

[0034]

175N BASE OILS		
SAMPLE	% BIODEGRADATION (21 DAYS) ¹	SD
A: Base Oil	76.93	1.452
B: Base Oil	62.01	1.379
C: Base Oil	51.04	1.657
G. ETHYLFLO 166	29.0	
X: VISTONE A30	85.31	0.408

¹ Based on analysis of triplicate inoculated test systems and triplicate poisoned test systems.

[0035] These data show that two different 100N oils were of biodegradability approaching 75%, and two different 100N oils were of biodegradability well above 75%; one approximating 85%. The Blue Angels in Germany, defines "readily biodegradable" as $>80\%$ in the CEC-L-33-T-82 test. The three 175N oils that were demonstrated had biodegradability values ranging between about 51% to about 77%.

[0036] The DWO base stocks, and lubricant compositions due to their high paraffinic content, >97.5 Vol.%, are also suitable as feedstocks for medicinal grade white oils. The following is exemplary.

Example 18

[0037] A dewaxed 60N base oil was subjected to mild hydrofining over a Ni-Mn-MoSO₄ bulk catalyst to produce an 80 wt.% level of conversion (i.e., 240°C , 600° psi H₂, 0.25 LHSV). The product readily passed the diagnostic "hot acid

test" for medicinal grade white oils.

[0038] It is apparent that various modifications and changes can be made without departing the spirit and scope of this invention.

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Claims

1. Biodegradable high performance hydrocarbon base oil useful as a lubricant in engine oil and industrial oil composition obtainable by a process which comprises
 - 10 contacting a 700°F+ paraffinic feed, or paraffinic feed containing 700°F+ components obtained from a Fischer Tropsch process, with hydrogen, over a dual functional catalyst, active for both hydroisomerization and hydrocracking, comprised of a Group VIII metal, or metals, on a support constituted of silica and alumina, to convert from 20 percent to about 50 percent, on a once through basis based on the weight of 700°F+ components of the feed, to produce a crude fraction containing 700°F+ materials rich in isoparaffins having from 6.0 to 7.5 methyl branches
 - 15 per 100 carbon atoms,
 - topping said crude fraction via atmospheric distillation to produce a residual bottoms fraction the initial boiling point of which boils between about 650°F and about 750°F,
 - dewaxing said bottoms fraction with a solvent and recovering a dewaxed oil, and
 - 20 fractionating said dewaxed oil with a vacuum to recover said biodegradable high performance hydrocarbon base oil.
 2. The process of claim 1 wherein the catalyst is comprised of a Group IB or Group VIB metal, or metals, or both a Group IB and Group VIB metal, or metals, in addition to the Group VIII metal, or metals.
 - 25 3. The process of claim 2 wherein the concentration of the metal, or metals, ranges from about 0.1 percent to about 20 percent, based on the total weight of the catalyst, the Group IB metal is copper, the Group VIB metal is molybdenum, and the Group VIII metal is palladium, platinum, nickel or cobalt.
 4. The process of claim 1 wherein the 700°F+ level of conversion of the paraffinic feed ranges from 25 percent to 40
 - 30 percent.
 5. The process of claim 1 wherein one or more viscosity grades of lubricant are produced from the solvent dewaxed oil by vacuum fractionation, and at least one of the fractions is
 - 35 hydrofined sufficiently to pass the diagnostic hot acid test to produce a medicinal grade white oil.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 02 3062

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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 14 November 2003	Examiner De Herdt, O
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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